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(54) Title: PROCESS FOR THE PRODUCTION OF CESIUM COMPOUNDS			
<pre> graph TD BIS[Barium Ion Source] --> SC1[Solubilized Cesium Compound + Ionic Impurities] HIS[Hydroxyl Ion Source] --> SC1 CIS[Carbonate Ion Source] --> SC2[Solubilized Cesium Compound + Residual Calcium Ions] SC1 --> IP1[Insoluble Precipitate(s)] SC2 --> IP2[Insoluble Precipitate(s)] IP1 --> PC[Purified Cesium Compound] IP2 --> PC </pre>			
(57) Abstract <p>Disclosed is a process for purifying a cesium compound which includes an ionic impurity comprising: calcium, sulfate, magnesium or mixtures thereof comprising: reacting impurities comprising calcium, sulfate, magnesium or mixtures thereof in a solution including the solubilized starting cesium compound with suitable precipitating agents to form an insoluble precipitate including the impurity or impurities. Preferred precipitating agents include barium ion to precipitate sulfate ionic impurities as barium sulfate; hydroxyl ion to precipitate magnesium ionic impurities as magnesium hydroxide and to precipitate calcium ionic impurities as calcium hydroxide; and carbon dioxide or carbonate ion to precipitate calcium ionic impurities as calcium carbonate. Also disclosed is a process for producing a predetermined cesium compound. The process comprises treating a cesium-including material with a suitable reagent to dissolve at least a portion of the cesium contained in the material and form a slurry; adding a base comprising slaked lime or calcium carbonate and, if necessary to produce the desired cesium compound, an acid including the anion of the predetermined cesium compound to the slurry comprising the dissolved cesium; and separating the predetermined cesium compound. In one embodiment of the invention, there is provided a process for producing a predetermined cesium compound from an ore comprising cesium aluminosilicate comprising: treating an ore comprising cesium aluminosilicate with an acid to form a slurry and dissolve at least a portion of the cesium contained in the ore; adding a base comprising slaked lime or calcium carbonate and a quantity of an acid including the anion of the predetermined cesium compound to the slurry comprising dissolved or solubilized cesium; and separating the predetermined cesium compound. A drilling fluid or heavy medium separation fluid comprising a purified cesium compound and having a specific gravity of between about 1.2 g/cm³ and about 2.5 g/cm³ and having less than 85 % by weight of the predetermined cesium compound on a solution basis is also disclosed.</p>			

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Process for the production of cesium compounds

Field Of The Invention

- The present invention relates to processes for purifying cesium compounds.
- 5 The present invention also relates to processes for the production or recovery of cesium from cesium-including materials, preferably in the form of a desired cesium compound such as a cesium salt.

Background of the Invention

- 10 Processes for recovering cesium, in the form of a cesium compound, from cesium-including materials such as pollucite and other cesium-including minerals have been reported in the technical literature.

One process which is reported involves leaching ground pollucite ore with strong sulfuric acid to obtain an extract including cesium alum, which is recovered by 15 crystallization.

Cesium alum is cesium aluminum sulfate hydrate. Its formula can be empirically expressed as $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, or $\text{Cs}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. The cesium alum contained in or crystallized from the sulfuric acid extracts of pollucite is typically contaminated with other metal ions such as rubidium, sodium, potassium, 20 magnesium and iron.

The cesium alum is then redissolved in water at an elevated temperature and reacted with an alkaline earth metal hydroxide, such as barium hydroxide or calcium hydroxide, to form an aluminum hydroxide precipitate together with precipitated barium sulfate or calcium sulfate. The cesium alum may alternatively be reacted with 25 ammonia to precipitate the aluminum as aluminum hydroxide. The cesium sulfate remains in the supernatant solution. The cesium can be recovered from the supernatant solution and converted into other cesium compounds.

U.S. Patent No. 3,207,571 to Berthold discloses a process for producing cesium compounds from aluminosilicate ore. German Patent DE 43 13 480 of 30 Hoffmann et al. discloses a process which avoids the use of barium compounds in the production of cesium salts from cesium alum. This process results in a product including calcium sulfate and magnesium.

One reported use for cesium compounds, such as cesium formate, is in high specific gravity drilling fluids for oil and gas wells. Bore hole turnings are known to 35 slow or stop the drilling process, and in some cases, plug the porous strata of the bore hole. Feedback data on the bore hole condition is limited in the regions of plugged strata thereby reducing the effectiveness of the drilling operation. High density fluids

having a specific gravity of about 1.8 and above have been used to convey the turnings to the surface. For wells having a depth greater than one mile, zinc bromide and mixtures with other salts have been utilized to improve the performance of the fluids. However, the nature of these materials renders them somewhat undesirable. One material which has been mentioned as a replacement for zinc bromide is cesium formate. Blends of cesium formate with other alkali metal formates are also mentioned. See European Patent No. 572 113.

A problem which may occur is the incompatibility of impurities found in cesium compounds such as cesium formate, with the various solutions, viscosifiers, and additives used in drilling fluids. For example, the presence of divalent impurities like calcium in cesium compounds may degrade the polymers present in the viscosifiers. The presence of divalent impurities is particularly harmful in high temperature and high pressure applications commonly found in deep well drilling where the viscosifier functions to suspend the bore hole turnings and act as a drilling lubricant.

Cesium compounds produced by the above described processes, however, do not avoid the problem of side reaction precipitates forming between divalent and multivalent cationic impurities and the carbonates present in the drilling environment or the corrosion effect of drilling equipment materials caused by sulfate ion impurities. Therefore, it would be advantageous to have a process for purifying cesium compounds produced by commercial processes.

Further, there has been a recognized need for a cesium compound having a substantially reduced level of divalent and multivalent cation impurities and sulfate ions and an improved process for its preparation.

25

Summary of the Invention

The aforementioned advantages, and others, are achieved by the processes of the present invention.

The present invention provides processes for purifying cesium compounds produced by heretofore known cesium production processes, and the processes of the present invention described herein. The purifying processes of the present invention may also be useful in purifying reclaimed cesium compounds, for example drilling/well servicing fluids comprising cesium formate.

30
35 The purifying processes of the present invention may be utilized to produce a cesium compound, including but not limited to cesium formate, cesium nitrate, cesium

chloride, cesium iodide, cesium bromide and cesium acetate comprising, on a dry weight basis:

less than 0.50% of a sulfate group, less than 0.3% of barium, calcium, or magnesium including compounds, and less than 0.2% of other multivalent cationic impurities.

- 5 Preferably the cesium compound further comprises, on a dry weight basis, less than 0.50% a chloride group and less than 0.3% of aluminum. The purifying processes of the present invention may also be utilized to produce a compound, including but not limited to cesium formate, cesium nitrate, cesium chloride, cesium iodide, cesium bromide and cesium acetate comprising, on a dry weight basis:

- 10 less than 1000 parts per million (ppm), preferably less than 500 ppm, more preferably less than 30 ppm sulfate;

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm calcium;

- 15 less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm barium; and

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm magnesium.

In a preferred embodiment, the low impurity levels of purified cesium formate render the material particularly advantageous for use in drilling fluids.

- 20 In addition the purifying process of the present invention may be utilized to produce a cesium sulfate compound comprising:

less than 0.3% of barium, calcium, or magnesium including compounds, and less than 0.2% of other multivalent cationic impurities. Preferably the cesium sulfate further comprises, on a dry weight basis, less than 0.50% a chloride group and less

- 25 than 0.3% of aluminum. The purifying processes of the present invention may also be utilized to produce a purified cesium sulfate compound comprising:

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm calcium;

- 30 less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm barium; and

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm magnesium.

- The present invention also provides processes for producing a predetermined cesium compound comprising: treating a cesium-including material with a suitable reagent to dissolve at least a portion of the cesium contained in the material and form a

compound may comprise, on a dry weight basis:

- less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm sulfate;

less than 1000 ppm, preferably less than 500 ppm, more preferably

slurry; adding a base comprising slaked lime or calcium carbonate and a quantity of an acid including the anion of the predetermined cesium compound to the slurry, if necessary to produce the predetermined cesium compound; and separating the predetermined cesium compound wherein the separation occurs in the presence of the remainder of the starting cesium-including material (the starting cesium-including material residues). The predetermined cesium compound may be further purified by the process for purifying cesium compounds of the present invention.

As used herein, the term "predetermined cesium compound" means a compound produced by combination of free cesium ion and an anion. Examples of cesium compounds which may be produced by the processes of the present invention include but are not limited to cesium formate, cesium sulfate, cesium chloride, cesium iodide and cesium nitrate. As explained in more detail below, in embodiments of the processes of the present invention, cesium sulfate may be produced directly from cesium alum without the need to add additional anion. In embodiments of the processes of the present invention utilized to produce cesium formate, cesium chloride, cesium iodide, cesium nitrate and other predetermined cesium compounds (other than cesium sulfate) a quantity of an acid including the anion of the predetermined cesium compound is utilized.

In accordance with yet another aspect of the present invention there is provided a fluid comprising a cesium compound and having a specific gravity of between about 1.2 g/cm³ and about 2.5 g/cm³ and having 10% to 100% by weight of the cesium compound on a dry salt basis, and less than 85% by weight of the cesium compound on a solution basis. Preferably the cesium compound comprises on a dry weight basis:

less than 0.50% of a chloride or sulfate group, less than 0.3% of aluminum, barium, calcium, or magnesium including compounds, and less than 0.2% of other multivalent cationic impurities. In an alternate embodiment of the fluid, the cesium compound may comprise, on a dry weight basis:

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm sulfate;

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm calcium;

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm barium; and

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm magnesium.

The purifying process of the present invention may be advantageously utilized to purify cesium compounds produced by heretofore known cesium production processes, and the cesium production processes of the present invention.

The cesium production processes of the present invention may be advantageously utilized to produce cesium compounds in an economic and efficient manner.

Further details relating to the present invention are described in the following
10 Detailed Description of the Invention.

Brief Description of the Drawings

In the Drawings:

Figure 1 is a block schematic diagram of an embodiment of the process for
15 purifying cesium compounds of the present invention.

Figure 2 is a block schematic diagram of another embodiment of the process for purifying cesium compounds of the present invention.

Figure 3 is a block schematic representation of an embodiment of a cesium production process of the invention.

20 Figures 4A - 4C illustrate block schematic representations of alternative embodiments of various aspects of a cesium production process of the invention.

Figure 5 is a block schematic representation of another embodiment of a cesium production process of the invention.

25 Detailed Description of the Invention

The present inventors have found an improved process for purifying cesium compounds. The purifying process is particularly advantageous for use in purifying cesium compounds produced by a process utilizing lime. The purifying processes of the present invention may be carried out on a commercial scale utilizing conventional
30 industrial scale mixing vessels and equipment for handling the cesium-including materials (e.g., ores) and strong acid and base solutions. The choice of the particular equipment utilized to practice the processes of the present invention is believed to be within the skill of one of ordinary skill in the art and therefore is not described below.

According to the present invention, an embodiment of a process for purifying
35 cesium compounds from a starting cesium compound which includes an ionic impurity

comprising: calcium, sulfate, magnesium or mixtures thereof comprises: reacting impurities comprising calcium, sulfate, magnesium or mixtures thereof present in a solution including the solubilized starting cesium compound with suitable precipitating agents to form an insoluble precipitate including the impurity or impurities. Preferred 5 precipitating agents include barium ion to precipitate sulfate ionic impurities (SO_4^{2-}) as barium sulfate; hydroxyl ion to precipitate magnesium ionic impurities as magnesium hydroxide and to precipitate calcium ionic impurities as calcium hydroxide; and carbon dioxide or carbonate ion to precipitate calcium ionic impurities as calcium carbonate. The insoluble precipitates may be separated from the purified cesium compound by 10 conventional techniques such as filtering and/or other suitable physical separation techniques, for example centrifugation. In an embodiment of the process of the present invention depicted schematically in Figure 1, the impurities in the solution including the solubilized starting cesium compound are first reacted with barium ion and hydroxyl ion precipitating agents and the resulting solution is reacted with carbon 15 dioxide or carbonate ion to precipitate any remaining calcium ionic impurities.

The source of barium ions and the source of hydroxyl ions may be the same or different. Suitable sources of barium ions include: barium hydroxide and soluble barium salts having an ion in common with the cesium compound being purified, for example barium formate in a process for purifying cesium formate. A preferred source 20 of barium ions is barium hydroxide. The barium ion source is employed in an amount sufficient, and reacted under conditions sufficient to precipitate at least a portion of the impurities. Preferably the barium ion source is employed in an amount, and reacted under conditions, sufficient to precipitate all or substantially all of the impurities. In a more preferred embodiment of the purifying process of the present invention, barium 25 ions are added in an amount approximately equal to the stoichiometric amount of sulfate ions determined to be in the solution. When barium hydroxide is utilized as the barium ion source, the insoluble precipitates may include barium sulfate, calcium hydroxide and/or magnesium hydroxide, depending on whether sulfate, calcium and magnesium ions are present in the starting cesium compound. The inventors note that it is possible 30 to form insoluble precipitates utilizing less than 0.12 kilogram of barium hydroxide is added to the solution per 1 kilogram of starting cesium compound contained in the solution.

Suitable sources of hydroxyl ions include: barium hydroxide, alkali hydroxides and calcium hydroxide with barium hydroxide being preferred. The hydroxyl ion 35 source is employed in an amount sufficient, and reacted under conditions sufficient to

precipitate at least a portion of the impurities. Preferably the hydroxyl ion source is employed in an amount, and reacted under conditions, sufficient to precipitate all or substantially all of the impurities. In a preferred embodiment of the purifying process of the present invention, hydroxyl ions are added in an amount sufficient to raise the pH of the resulting solution to 11.5 or greater. In accordance with the process of the present invention, when the pH of the resulting solution is raised to 11.5 or greater, magnesium ions in the solution will precipitate, when the pH of the resulting solution is raised to greater than 13, calcium ions in the solution will precipitate.

As indicated above, the purifying process of the present invention may further comprise reacting carbonate ions or carbon dioxide with the solution including the solubilized starting cesium compound to form an insoluble precipitate including at least a portion of any calcium ions remaining in the solution. Suitable carbonate ion sources include, but are not limited to, alkali carbonates such as cesium carbonate, potassium carbonate or sodium carbonate. The carbonate ion source is employed in an amount sufficient, and reacted under conditions sufficient to precipitate at least a portion of the calcium ions remaining in the solution. Preferably the carbonate ion source is employed in an amount, and reacted under conditions, sufficient to precipitate all or substantially all of the calcium ions remaining in the solution.

In general, the extent to which the purification of the cesium compound is carried out is dependent on the end use application for the purified cesium compound.

The foregoing process steps of the process for purifying a cesium compound of the present invention are particularly well suited to purifying cesium compounds such as cesium formate, cesium chloride, cesium iodide, cesium nitrate, cesium bromide or cesium acetate. These cesium compounds, and others such as cesium sulfate, may be produced from cesium-including materials, including naturally occurring minerals or ores, such as pollucite, solutions including cesium aluminum sulfate, and other materials, e.g., spent catalysts or residues comprising cesium fluoride or cesium sulfate.

A solution including solubilized cesium formate, cesium chloride, cesium iodide, cesium nitrate, cesium bromide or cesium acetate may be produced by a process of the present invention comprising:

treating a cesium-including material with a suitable reagent to dissolve at least a portion of the cesium contained in the material and form a slurry comprising cesium alum, cesium sulfate or cesium fluoride;

- adding a base comprising slaked lime or calcium carbonate and an acid including an anion of cesium formate, cesium chloride, cesium iodide, cesium nitrate, cesium bromide or cesium acetate to the slurry to form solubilized cesium formate, cesium chloride, cesium iodide, cesium nitrate, cesium bromide or cesium acetate; and
- 5 separating the solubilized cesium compound solution in the presence of the remainder of the starting cesium-including material.

An alternate embodiment of the purifying process of the present invention is preferred for purifying a cesium sulfate compound. This alternate embodiment is depicted schematically in Figure 2.

- 10 According to the present invention, a process for purifying cesium sulfate from a starting cesium sulfate compound which includes an ionic impurity comprising: calcium, magnesium or mixtures thereof comprises: reacting impurities comprising calcium, magnesium or mixtures thereof present in a solution including the solubilized starting cesium sulfate compound with suitable precipitating agents to form an
- 15 insoluble precipitate including the impurity or impurities. Preferred precipitating agents include hydroxyl ion to precipitate magnesium ionic impurities as magnesium hydroxide and to precipitate calcium ionic impurities as calcium hydroxide; and carbon dioxide or carbonate ion to precipitate calcium ionic impurities as calcium carbonate. The insoluble precipitates may be separated from the purified cesium compound by
- 20 conventional techniques such as filtering and/or other suitable physical separation techniques, for example centrifugation. In an embodiment of the process of the present invention depicted schematically in Figure 2, the impurities in the solution including the solubilized starting cesium compound are first reacted with an hydroxyl ion precipitating agent and the resulting solution is reacted with carbon dioxide or
- 25 carbon ion to precipitate any remaining calcium ionic impurities.

- Suitable sources of hydroxyl ion (bases) include hydroxides of a metal selected from group 1A and 2A of the Periodic Table of the Elements and mixtures thereof. For example the source of hydroxyl ion (base) may comprise lime, slaked lime, potassium hydroxide, sodium hydroxide, cesium hydroxide or a mixture thereof, with slaked lime being preferred. The hydroxyl ion source is employed in an amount sufficient, and reacted under conditions sufficient to adjust the pH of the solution to an extent so as to precipitate at least a portion of the impurities. In accordance with the process of the present invention, when the pH of the resulting solution is raised to 11.5 or greater, magnesium ions in the solution will precipitate.

As indicated above, this embodiment of the purifying process of the present invention may further comprise reacting carbonate ions, or carbon dioxide, with the solution including the solubilized starting cesium sulfate to form an insoluble precipitate including at least a portion of any calcium ions remaining in the solution.

- 5 Suitable carbonate ion sources include, but are not limited to, alkali carbonates such as cesium carbonate, potassium carbonate or sodium carbonate. The carbonate ion source is employed in an amount sufficient, and reacted under conditions sufficient to precipitate at least a portion of the calcium ions remaining in the solution. Preferably the carbonate ion source is employed in an amount, and reacted under conditions, sufficient to precipitate all or substantially all of the calcium ions remaining in the solution.
- 10

A solution including solubilized cesium sulfate may be produced by a process of the present invention comprising:

- 15 treating a cesium-including material with a suitable reagent to dissolve at least a portion of the cesium contained in the material and form a slurry comprising cesium alum;
- 20 adding a base comprising slaked lime or calcium carbonate to the slurry comprising dissolved cesium to form a solubilized cesium sulfate compound; and separating the solubilized cesium sulfate compound solution in the presence of the remainder of the starting cesium-including material.

- The purifying processes of the present invention may be utilized to purify cesium compounds produced by a process of the present invention or by other cesium compound production processes. In many cesium production processes the solution comprising the solubilized cesium compound will exist at a stage in the production process prior to separation and recovery of the cesium compound. A purifying process of the present invention may be performed at this stage as part of the cesium production process. If necessary, in other applications of a purifying process of the present invention, a solution comprising the solubilized cesium compound may be formed by solubilizing the cesium compound utilizing known techniques.
- 30 The purifying processes of the present invention may be utilized to produce a cesium compound, including but not limited to cesium formate, cesium nitrate, cesium chloride, cesium iodide, cesium bromide and cesium acetate comprising, on a dry weight basis:
 - 35 less than 0.50% of a sulfate group, less than 0.3% of barium, calcium, or magnesium including compounds, and less than 0.2% of other multivalent cationic

impurities. Preferably the cesium compound further comprises, on a dry weight basis, less than 0.50% a chloride group and less than 0.3% of aluminum.

The purifying processes of the present invention may also be utilized to produce a cesium compound, including but not limited to cesium formate, cesium nitrate, cesium chloride, cesium iodide, cesium bromide and cesium acetate comprising, on a dry weight basis:

less than 1000 parts per million (ppm), preferably less than 500 ppm, more preferably less than 30 ppm sulfate;

10. 30 ppm calcium;

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm barium; and

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm magnesium.

15 In addition, the purifying process of the present invention may be utilized to produce a cesium sulfate compound comprising:

less than 0.3% of barium, calcium, or magnesium including compounds, and less than 0.2% of other multivalent cationic impurities. Preferably the cesium sulfate further comprises, on a dry weight basis, less than 0.50% a chloride group and less than 0.3% of aluminum. The purifying process of the present invention may also be utilized to produce a cesium sulfate compound comprising:

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm calcium;

25 30 ppm barium; and

less than 1000 ppm, preferably less than 500 ppm, more preferably less than 30 ppm magnesium.

In accordance with another aspect of the invention there is provided a high specific gravity fluid which comprises an aqueous mixture on a dry salt basis of 30 between 10 and 100% of a cesium compound which has been purified in accordance with one of the processes of the present invention. The high specific gravity fluid produced has varied applications including use as a drilling fluid or in mineral extraction processes. The high specific gravity fluid contemplated by this invention has a specific gravity of between 1.2 g/cm³ and about 2.5 g/cm³ and on a dry salt basis and comprises less than 0.50% (by weight) of chloride or sulfate anions; less

than 0.3% (by weight) of materials such as aluminum, barium, calcium, or magnesium including compounds; and less than 0.2% (by weight) total of other multivalent cationic impurities. In a preferred embodiment the cesium compound comprises:

- less than 1000 ppm, more preferably less than 500 ppm, even more preferably
- 5 less than 30 ppm sulfate;
- less than 1000 ppm, more preferably less than 500 ppm, even more preferably less than 30 ppm calcium;
- less than 1000 ppm, more preferably less than 500 ppm, even more preferably less than 30 ppm barium; and
- 10 less than 1000 ppm, more preferably less than 500 ppm, even more preferably less than 30 ppm magnesium.

In another aspect of the present invention, the present inventors have also found an improved process for preparing cesium compounds from cesium-including materials, including naturally occurring minerals or ores, such as pollucite, solutions including cesium aluminum sulfate, and other materials, e.g., spent catalysts or residues comprising cesium fluoride or cesium sulfate.

The cesium production processes of the present invention may be carried out utilizing conventional industrial scale mixing vessels and equipment for handling the cesium-including materials (e.g., ores) and strong acid and base solutions. The choice 20 of the particular equipment utilized to practice the processes of the present invention is believed to be within the skill of one of ordinary skill in the art and therefore is not described below.

One embodiment of a process of the present invention comprises treating a cesium-including material with a suitable reagent to dissolve at least a portion, and 25 preferably all or nearly all, of the cesium contained therein and form a slurry, adding a base comprising slaked lime or calcium carbonate, adding an acid including the anion of a predetermined cesium compound to the slurry comprising dissolved cesium if necessary to produce the desired cesium compound, reacting the mixture to produce the predetermined cesium compound and separating the predetermined cesium 30 compound from the mixture in the presence of the remainder of the starting cesium-including material. Preferably, as part of the separation step or steps, the predetermined cesium compound is further purified to remove at least a portion of any remaining trace impurities.

With reference to an embodiment of the invention illustrated in Figure 3, a 35 cesium-including material, such as pollucite ore, and an acid suitable for digesting the

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- ore and dissolving at least the cesium present therein are combined to form a slurry. Suitable acids include, but are not limited to, mineral acids (e.g., sulfuric acid) and hydrofluoric, hydrobromic, and hydrochloric acids. Water may also be added to assist in the dissolution of the cesium and any aluminum and other alkali metals that may be 5 present in the ore. To further assist in dissolving the cesium and any other alkali metals and aluminum in the ore, the ore may be comminuted prior to its being combined with the acid. In a preferred embodiment, the ore is ball milled to approximately -200 mesh particle size.

In one embodiment the amount of acid mixed with the ore is equal to or in 10 excess, preferably greater than 110%, of the stoichiometric amount of acid theoretically required to dissolve all of the cesium and any aluminum and/or other alkali metal(s) present in the ore. (The cesium, aluminum, and alkali metal content of the ore can be adequately determined by assaying the ore.) In another embodiment of the process of the present invention, a 45% (by weight) solution using 93% (by 15 weight) sulfuric acid is employed in a ratio of between 0.2 to 0.8 in kilos of ore per liters of acid solution.

As will be appreciated by those skilled in the art, the acid used to form the slurry may be a single acid or a mixture of acids. The amount of acid and/or the choice of the acid or acid mixture is dependent on the composition of the ore or residue 20 material from which cesium is being extracted. While the following examples and discussions refer to pollucite ore, as used herein, the term "cesium-including materials" shall include any naturally occurring cesium-including minerals or ores, as well as other solids or liquid materials comprising cesium, including process residues such as spent catalyst material.

25 In a preferred embodiment, cesium alum is formed as an intermediate in the process. Formation of the cesium alum intermediate requires the presence of sulfate ions and aluminum ions. If the acid or acid mixture does not include sulfuric acid, a source of sulfate ions can be added to facilitate the formation of a cesium alum intermediate. If the cesium-including material does not include aluminum, a source of 30 aluminum ions can be added to facilitate cesium alum formation.

As shown in Figure 4A, the acid may be recycled into the ore digestion vessel which will reduce the amount of acid that is used.

The digestion of the ore and acid mixture is preferably conducted under 35 conditions and for a time period sufficient to extract a sufficient amount of cesium from the ore to render the overall process commercially efficient. More preferably, the

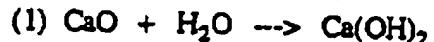
- reaction is permitted to continue until at least approximately 90% of the cesium is dissolved from the ore, as may be determined from analysis of the spent ore. In one embodiment of the invention, the reaction of the ore and acid is conducted with hot sulfuric acid at a temperature of from about 115° C to about 200° C, and preferably at a 5 temperature of approximately 120° C. The reaction (or digestion) period is preferably at least 4 hours, and more preferably approximately 16 hours. When a shorter digestion period or a lower sulfuric acid temperature is employed, cesium dissolution from the ore is less complete. During the reaction, the hot digestion liquor becomes increasingly more paste-like in consistency. Additional water may be added to 10 maintain the original volume of the mixture. If the evaporated water is not replaced the slurry may eventually solidify. Optionally, the original volume of the mixture can be maintained by refluxing. When aluminum is present in the ore, the ore/sulfuric acid slurry comprises solubilized cesium aluminum sulfate (also referred to herein as cesium alum), formed from the cesium dissolved from the ore. When an excess of 15 acid is present after achieving the desired level of digestion, the slurry may optionally be diluted with water and cooled to approximately 30° C to crystallize cesium alum. The remaining sulfuric acid in the mixture is preferably decanted and recycled; and the remaining spent ore and cesium alum can optionally be reslurried. (See again Figure 2A).
- 20 Reslurrying may be accomplished by adding water to the spent ore and cesium alum. The solubility of the cesium slum in the reslurry is primarily a function of water volume and temperature employed and therefore the conditions for recrystallizing the cesium alum may be readily determined by those skilled in the art. In a preferred embodiment, the temperature of the reslurry after water addition is approximately 100° C.
- 25 Referring to Figure 4B, those of ordinary skill in the art will recognize that cesium alum and ultimately the predetermined cesium compound may be further purified at this point in the process by recrystallizing the solubilized cesium aluminum sulfate in the slurry for further processing. The recrystallization process may be repeated as many times as desired to further purify the cesium alum.

30 Referring again to Figure 3, a base comprising slaked lime or calcium carbonate and optionally, an acid including the anion of the predetermined cesium compound are added to the slurry and spent ore, either together or sequentially in either order, to adjust the pH to about 4 to about 9. If a cesium sulfate compound is

the desired product of the process, the addition of acid is not necessary as cesium sulfate may be separated directly from the cesium alum.

The slaked lime is prepared by contacting lime (calcium oxide) with water ("slaking"). The "slaking" reaction is provided by equation (1).

5



By preslaking the lime, the pH can be controlled so that the level of aluminum and calcium impurities in the solubilized cesium compound are minimized.

In a preferred embodiment, the base comprises slaked lime. The slaked lime is allowed to react with the slurry and acid under conditions sufficient, and for a 10 sufficient time period, to allow precipitation of aluminum, any silica and/or iron dissolved in the liquid component of the slurry. As provided above, to achieve the precipitation of the aluminum hydroxide, sufficient base is added to the mixture to achieve a pH in the range of about 4 to about 9. In a more preferred embodiment, base is added to achieve a pH of about 7 to about 8. In this more preferred pH range, 15 substantially complete precipitation of solubilized aluminum is obtained.

After the slaked lime is added, the spent ore, precipitated aluminum hydroxide, and precipitated calcium sulfate are separated from the mixture including the solubilized cesium ions. The separation may be accomplished by any known means, such as by filtering.

20

In accordance with the invention, the spent ore or undissolved portion of the cesium-including material is utilized as a filtration aid for separation of aluminum hydroxide which is formed by the addition of base to the acid digested ore or treated cesium-including material. The use of the spent ore or undissolved material improves the filtration rate of the aluminum hydroxide that is formed as well as easing the 25 washability of the solids to maximize cesium recovery. Inclusion of the spent ore also improves compressibility and dewatering of solids.

25

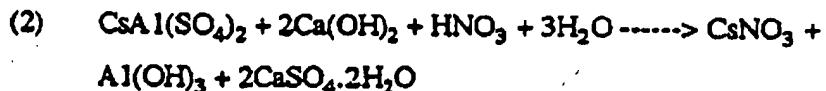
In another preferred embodiment, slaked lime and calcium carbonate are employed together. The slaked lime and calcium carbonate, whether used alone or in combination, may also be used with one or more additional bases comprising an ion of a metal selected from groups 1A (alkali metals) and 2A (alkaline earth metals) of the Periodic Table of the Elements and mixtures thereof. Examples of such additional bases include KOH, NaOH, K₂CO₃, Na₂CO₃, RbOH, Rb₂CO₃, LiOH, Li₂CO₃, Mg(OH)₂, MgCO₃, Cs₂CO₃, and CsOH.

30

The selection of the acid used to produce the predetermined cesium compound 35 which is added to the slurry (and any optional reslurry) depends on the particular

cesium compound(s) desired. For example, if one desires to produce cesium nitrate, a combination of slaked lime and nitric acid are added in an amount sufficient to adjust the pH of the mixture to approximately 7 to 8. It is believed that the reaction proceeds according to equation (2) and that similar reactions will occur with other acids:

5



As discussed above, the addition of a sulfate anion in acid form, is not necessary to produce cesium sulfate since the sulfate ion will already exist in the cesium alum 10 including solution.

Examples of acids suitable for use in preparing a predetermined cesium compound (or cesium salt), include but are not limited to the acids set forth in Table 1:

15

Table 1: Acids/Cesium Compounds

Acid Added	Cesium Compound Product
Nitric Acid (HNO_3)	Cesium Nitrate (CsNO_3)
Formic Acid (HCOOH)	Cesium Formate (CsCOOH)
Formic Acid (as calcium formate) ($\text{Ca}(\text{OOCH})_2$)	Cesium Formate (CsCOOH)
Hydrochloric Acid (HCl)	Cesium Chloride (CsCl)
Hydrobromic Acid (HBr)	Cesium Bromide (CsBr)
Acetic Acid ($\text{HC}_2\text{H}_3\text{O}_2$)	Cesium Acetate ($\text{CsC}_2\text{H}_3\text{O}_2$)
Hydroiodic Acid (HI)	Cesium Iodide (CsI)

As will be recognized by those of ordinary skill in the art, Table 1 provides a list of examples of acids that can be used and is not to be construed as a complete or exhaustive list of suitable acids. Rather, suitable acids include any acids which will react with the cesium ions to yield the cesium compound desired as the end product.

As will also be recognized by those of ordinary skill in the art from Table 1, it is possible to substitute certain salts for the acid. For example, as shown, calcium formate may be added instead of formic acid to produce a cesium formate end product.

Referring to Figure 4C, as part of the separation and recovery step, the 25 solubilized cesium compound may be purified or "polished" to remove trace impurities according to an embodiment of the purifying process of the present invention. As

depicted in Figure 4C, soluble compounds of barium and soluble compounds of carbonate (or carbon dioxide) may be added to the solution mixture including solubilized ions of cesium and the anion of the predetermined cesium compound.

Typically, for purposes of polishing, less than 0.12 kilogram of barium hydroxide is

- 5 added per 1 kilogram of cesium compound contained in the solution. Insoluble barium sulfate, calcium hydroxide, and magnesium hydroxide formed as a result of the polishing step may be removed by filtration. Residual calcium ions in solution may be removed through the addition of alkali carbonates such as cesium carbonate, potassium carbonate, or sodium carbonate, or by treatment with carbon dioxide, to precipitate
- 10 insoluble calcium carbonate. The alkali carbonate is employed in an amount sufficient to precipitate all calcium ions present in the solution mixture. The extent to which the purification of the predetermined cesium compound is carried out is dependent on the end use application for the cesium compound.

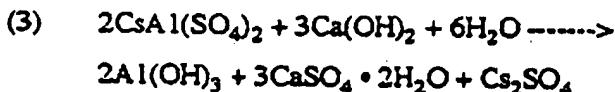
- After polishing, the solution including the dissolved cesium compound has an elevated pH of greater than 11. In order to improve the recovery of the cesium compound, an additional quantity of acid (of the type employed to form the predetermined cesium compound) is added to adjust the pH of the solution to a desired pH. The desired pH is dependent upon intended use or application. The cesium compound may then be recovered or separated, e.g., by driving off the water through heating.
- 15
 - 20

In the process of the invention, the predetermined cesium compound can be recovered as a solid or in solution, or as a solid or solution mixture including the predetermined cesium compound and one or more compounds comprising a different metal (e.g., alkali metals) and the anion of the predetermined cesium compound.

- 25 Referring now to Figure 5, there is illustrated an embodiment of the present invention wherein the base comprising slaked lime or calcium carbonate and acid including the anion of the predetermined cesium compound are added after the ore/acid digestion slurry has been treated with a first quantity of base. As discussed above and illustrated in Figure 3, ore which has been preferably ground to a mesh of -200, is
- 30 mixed or contacted with a suitable acid (e.g., sulfuric acid) and water in a process tank for dissolution of cesium and aluminum from the ore. The quantity of acid utilized in this step is preferably at least a stoichiometric quantity with respect to group 1A elements of the Periodic Table of Elements and aluminum contained in the ore. Water may be added to maintain the original volume. While not shown, the embodiment of
- 35 the invention illustrated in Figure 5 may further include cooling the hot digestion slurry

to obtain cesium alum and spent ore to crystallize the cesium alum, decanting the supernatant liquid which may include excess unreacted acid, and reslurrying the crystallized cesium alum and spent ore in water. Even if no excess acid is present, the crystallization and reslurry steps may be performed.

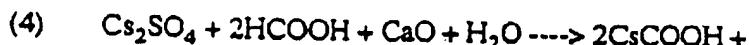
- 5 Referring again to Figure 5, the first quantity of base is mixed with the hot digestion slurry or alternatively, with the reslurry of cesium alum and spent ore, to adjust the pH to about 4 to about 9. The base comprises an ion of a metal selected from groups 1A and 2A of the Periodic Table of the Elements (e.g., slaked lime, calcium carbonate, lime, potassium hydroxide, sodium hydroxide, potassium
10 carbonate, sodium carbonate) and mixtures thereof. The base is allowed to react with the slurry or alternatively, the reslurry under conditions sufficient, and for a sufficient time period, to allow precipitation of the aluminum as aluminum hydroxide (Al(OH)_3); to allow precipitation of any silica and iron dissolved in the slurry or reslurry and to allow the formation of solubilized cesium sulfate. It is believed that the
15 precipitation generally proceeds according to the reaction illustrated in equation (3):

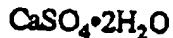


- 20 After the addition of slaked lime and the formation of solubilized cesium sulfate, the principal undissolved solids, e.g., precipitated aluminum hydroxide, precipitated calcium sulfate, and spent ore, are separated from the liquid component of the mixture. The liquid component includes crude cesium sulfate. The separation may be accomplished by any means known to the art, such as by filtering.

25 The inventors have discovered that the spent ore facilitates the filtering, washing, and dewatering characteristics of the precipitated Al(OH)_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ cake much like the enhanced filter throughout achieved by adding granular silica as a filtering aid.

- 30 A second base comprising slaked lime or calcium carbonate and an acid including an anion of the predetermined cesium compound are then added to the solubilized cesium sulfate. The reaction mechanism proceeds in accordance with the mechanism identified in equation (4) below:





- A slight excess of slaked lime can be added to achieve a pH sufficient to precipitate as magnesium hydroxide at least a portion, and preferably all or nearly all, 5 of any trace quantities of soluble magnesium present in the mixture to facilitate its removal by known separation techniques.

The acid is selected to contain the anion of the cesium compound desired as an end product. Examples are set forth in Table 1.

- The second base may further include base(s) comprising an ion of a metal 10 selected from groups 1A and 2A of the Periodic Table of the Elements and mixtures thereof. For example, the second base may comprise slaked lime or calcium carbonate, or slaked lime and/or calcium carbonate and one or more of the following bases: potassium hydroxide, sodium hydroxide, potassium carbonate and sodium carbonate.
- 15 To further purify the cesium compounds obtained by this embodiment, an embodiment of the purifying process of the present invention may be utilized in the same manner as discussed above.

- After polishing (purifying), the solution including the dissolved cesium compound has an elevated pH of greater than 11. In order to improve the recovery of 20 the cesium compound, an additional quantity of acid (of the type employed to form the predetermined cesium compound) is added to adjust pH of the solution to a desired pH. The desired pH is dependent upon intended use or application. The cesium compound may then be recovered or separated, e.g., by driving off the water through heating.

- 25 In the process of the invention, the predetermined cesium compound can be recovered as a solid or in solution, or as a solid or solution mixture including the predetermined cesium compound and one or more compounds comprising a different metal (e.g., alkali metals) and the anion of the predetermined cesium compound.

- 30 A range of cesium compounds of varying composition and purity which have been purified or produced and purified in accordance with the present invention are suitable for use as drilling fluids or heavy medium separation fluids. Alternatively, salts of other metals such as sodium or potassium can be coformed with the predetermined cesium compounds by adding such ions to the solution mixtures comprising solubilized cesium at any step of the process. For example, in one 35 embodiment, a cesium formate is produced by the process of the invention and sodium

formate or potassium formate are co-formed therewith in order to produce a mixed salt product. The composition of the salt or salt mixture produced is dependent on the anion of the acid and cation(s) of the base(s) utilized and the amounts thereof which are reacted with the solubilized cesium sulfate or with the solubilized cesium alum.

5 The features of the invention are further disclosed and represented by the following non-limiting Examples. The high specific gravity fluid may further comprise compounds of sodium or potassium where the anion of the compound is the same as that of the cesium compound included in the fluid.

Chemical analysis of the cesium compounds was performed using
10 conventional gravimetric analysis, emissions spectrographic analysis and atomic absorption techniques, readily known to those skilled in the art.

Example 1

This example illustrates the production of cesium formate via a one step
15 reaction and the purifying of the cesium formate utilizing a process of the present invention.

A 4 liter glass beaker was loaded with 444 grams of ground pollucite ore of nominally -200 mesh, 670 ml water, and 310 ml 98% by weight H₂SO₄. This represents about an 82% excess of acid above the stoichiometric requirements for
20 dissolution of alkali metals and aluminum from the ore. The mixture was continually mixed while heating at approximately 115° C for 16 hours. The leach volume was maintained by adding water.

After 16 hours, the slurry was diluted to a volume of 2200 ml with water, reheated to about 80-90° C, then cooled to room temperature. A decant of 940 ml was taken to remove most of the remaining unreacted H₂SO₄ acid. Nine hundred (900) ml of water were then added to reslurry the spent ore and crystallized cesium alum and the reslurry mixture was then heated to 80° C with stirring.

30 A slurry of slaked lime, made from 185 grams of calcium oxide and 700 ml water, was added to the heated reslurry mixture of cesium alum and spent ore along with 30 ml of 88% (by weight) formic acid. After these additions, the pH of the resulting mixture was 7.5. The mixture was heated to about 70° C and stirred for 1 hour.

The liquid component of the mixture (which contains the solubilized cesium formate) was then separated from the spent ore and the Al(OH)₃ and CaSO₄ precipitates by filtration. The filtered residue weighed 736 grams on a dry weight
35

basis. A wash of 600 ml of boiling water was applied to the filtered solids. The filtrates including the solubilized cesium formate were combined and mixed first with 38 grams $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ to remove residual SO_4^{2-} ; then with 15 grams Cs_2CO_3 to remove residual calcium ions. The solubilized cesium formate product was then 5 filtered to separate out barium sulfate, calcium carbonate, calcium hydroxide, and magnesium hydroxide. The filtrate was then analyzed and found to contain the following chemical make-up. (Values are recorded on a part per million on a dry weight basis of cesium formate product.)

10	Rb	9500 ppm
	K	500 ppm
	Na	7900 ppm
	Li	90 ppm
	Ca	20 ppm
15	C1	500 ppm
	SO_4	<100 ppm
	Al	50 ppm
	Ba	50 ppm
	Fe	4 ppm
20	Mg	1 ppm

The overall extraction yield was approximately 85%.

The cesium formate including filtrate was next mixed with a minimal amount of 88% (by weight) formic acid (less than 1 ml) to adjust the solution to a pH of from 25 about 6 to about 7. The cesium formate filtrate was then evaporated to a final volume of 53 ml; which had a density of 2.20 g/ml (approximately 79% CsCOOH).

Example 2

This example also illustrates the production of cesium formate and the purifying of the cesium formate utilizing a process of the present invention.

A 4 liter glass beaker was loaded with 444 grams of pollucite ground to -200 mesh, 670 milliliters (ml) water, and 310 ml 98% H₂SO₄. The mixture was mixed and heated to approximately 115° C for 16 hours. The leach volume was maintained with added water.

After 16 hours, the slurry was diluted to a volume of 2200-2500 ml with water, reheated, then cooled to room temperature. A decant of 1135 ml was taken to remove most of the remaining H₂SO₄ acid. The remaining cesium alum plus spent ore was reslurried with approximately 800 ml water, and heated to approximately 70° with stirring.

A slurry of slaked lime made from 150 grams of calcium oxide in approximately 500 ml water was added and a pH of 7-8 was obtained. The slurry was mixed for 1 and 1/2 hours at 90° C, cooled to 60° C, and then filtered to separate the insoluble solids including aluminum hydroxide, calcium sulfate, and spent ore. On a dry basis, the insolubles separated from the slurry weighed 675 grams.

The resulting Cs₂SO₄ filtrate plus wash water was heated to 70° C, and a mixture of 20 grams of calcium oxide in 100 ml of water, and 28 ml 88% (by weight) formic acid was added with mixing. An additional slurry of 2 grams calcium oxide in minimal water was added to raise the pH to above 11.5 to precipitate magnesium hydroxide.

The mixture was heated to 70° C and mixed for 1.5 hours, followed by filtering and washing of the collected solids with water. The cesium formate filtrate was then purified by the following steps:

The cesium formate filtrate was mixed with 20 grams Ba(OH)₂ • 8 H₂O to remove residual SO₄⁻² ions as BaSO₄, and then with 20 grams Cs₂CO₃ to remove residual calcium as CaCO₃. The BaSO₄ precipitate was filtered out prior to the treatment with Cs₂CO₃. After the CaCO₃ precipitate was filtered out; the final purified or polished CsCOOH filtrate was analyzed and determined to have the following chemical make-up:

Rb 6000 ppm

K 270 ppm

Na 4500 ppm

	Li	25 ppm
	Ca	45 ppm
	Cl	415 ppm
	SO ₄	< 80 ppm
5	Al	25 ppm
	Fe	5 ppm
	Ba	100 ppm
	Mg	3 ppm

The overall extraction yield was approximately 80%.

- 10 The cesium formate filtrate was mixed with a minimal amount of 88% formic acid (by weight) (less than 1 ml) to adjust the solution to a pH of between 6 and 7. The cesium formate filtrate was evaporated to a final volume of 42 mls; which had a density of 2.34 g/ml (approximately 83% CsCOOH).

15 Example 3

This example illustrates the production of cesium sulfate and the purifying of the cesium sulfate utilizing a process of the present invention.

- A 4 liter glass beaker was loaded with 444 grams of pollucite ground to -200 mesh, 670 mls water, and 310 ml 98% H₂SO₄. The mixture was mixed and heated to approximately 115° C for 16 hours. The leach volume was maintained with added water so that an acceptable solids to liquids ratio was maintained. After 16 hours, the slurry was diluted to a volume of approximately 1800 mls with water, reheated, and then cooled to room temperature. A decant of 960 mls was taken to remove most of the remaining H₂SO₄ acid. The remaining cesium alum plus spent ore was reslurried with approximately 1000 mls water, and heated to about -80° C with stirring. A slurry of slaked lime composed of 160 grams of calcium oxide in approximately 300 mls water was added to heated solution of cesium alum and spent ore to achieve a pH of 7.5. The slurry was mixed for 2 hrs. at 80° C, cooled to 60° C, and filtered. The aluminum hydroxide, calcium sulfate and spent ore, on a dry basis, weighted 723 grams. The resulting Cs₂SO₄ filtrate plus wash water was heated to 70° C, and mixed with 25 grams Cs₂CO₃ was added to remove residual calcium as CaCO₃. CsOH was added in lieu of calcium hydroxide to raise the solution pH to 12 in order to precipitate Mg as Mg(OH)₂. After the CaCO₃ and Mg(OH)₂ precipitates were filtered out, the final Cs₂SO₄ filtrate was analyzed. The overall extraction yield was approximately

80%. The final Cs_2SO_4 liquor analyzed on a dry cesium sulfate basis had the following chemical make-up:

	Rb	7350 ppm
	K	1020 ppm
5	Na	5640 ppm
	Li	85 ppm
	Ca	17 ppm
	Al	5 ppm
	Fe	1 ppm
10	Mg	170 ppm
	Si	75 ppm
	Ba	<10 ppm

The final cesium sulfate filtrate was further treated by adding a few drops of a cesium hydroxide solution (50% by weight) to the filtrate and then resifting the 15 treated filtrate using Whatman fine filter paper. This additional treatment of the filtrate further reduced the magnesium content from 170 ppm to less than 10 ppm.

Example 4

This example illustrates the production of cesium nitrate and the purifying of 20 the cesium nitrate utilizing a process of the present invention.

A 2500 gallon process tank was loaded with 350 gallons water and 175 gallons 93% technical grade H_2SO_4 . Two thousand (2000) pounds of pollucite ore ground to -200 mesh were added with mixing. The mixture was reacted at approximately 115°- 120°C for 16 hours. The leach volume was maintained with added water. After 16 25 hours, the slurry was diluted to a volume of about 2000 gallons with water, reheated to 90°C, then cooled to room temperature. A decant of about 1500 gallons was taken to remove most of the remaining H_2SO_4 . The remaining cesium alum plus spent ore was reslurried with about 1400 gallons of water, heated to 90°C with agitation, and filtered through a filter press to remove the spent ore. 200 gallons of water was also 30 sent through the filter press was a washing step. The hot cesium alum solution including wash water was evaporated to a volume of about 1300 gallons, and allowed to cool to room temperature. A decant of about 1000 gallons was taken. The cesium alum was recrystallized a second time for further purification. The purified cesium alum reslurried in 1000 gallons water and heated. A slurry of 266 pounds of calcium 35 hydroxide slaked in approximately 125 gallons water was added to the purified

reslurry to achieve a pH of 8.1. The slurry was mixed for approximately 1 hour at 80°C, cooled to about 60°C, and filtered. The result Cs₂SO₄ filtrate plus water was heated to about 80°C, and a slurry of slaked lime comprising 80 pounds of calcium hydroxide in 125 gallons of water, and 199 pounds of 70% HNO₃ was added with 5 mixing. the pH of the mixture was measured to be >11.5. The mixture was stirred 2 hours, followed by filtering to remove insolubles such as calcium sulfate, calcium hydroxide, and magnesium hydroxide. The Cs₂NO₃ filtrate was evaporated to about 400 gallons. About 65 pounds of Ba(OH)₂ ·8H₂O was added to remove residual SO₄⁻² as BaSO₄. Then, 30 pounds Cs₂CO₃ was added to remove residual calcium as 10 CaCO₃. After barium sulfate, calcium hydroxide, and calcium carbonate were filtered out as precipitate, the CsNO₃ filtrate was pH adjusted to about 7 with HNO₃, and heated to evaporate water. The result product was 312 pounds of CsNO₃ crystals.

The dried CsNO₃ contained the following chemical make-up:

15	Rb	225 ppm
	K	1 ppm
	Na	2ppm
	L	<1 ppm
	Al	<1 ppm
20	Ba	25 ppm
	Ca	8 ppm
	Mg	<1 ppm
	Si	1 ppm
	SO ₄	<100 ppm
25	Cl	<50 ppm

Example 5

This example illustrates the production of cesium sulfate and the purifying of the cesium sulfate utilizing a process of the present invention.

30 A 2500 gallon process tank was loaded with 350 gallons water and 175 gallons 93% technical grade H₂SO₄. This amounted to an 80% excess of H₂SO₄ over the stoichiometric requirements. 2000 pounds of pollucite ore, ground to -200 mesh was added with mixing. the mixture was reacted at approximately 115°C-120°C for 16

hours. The leach volume was maintained with added water. After 16 hours, the slurry was diluted to a volume of 2000 gallons with water, heated to 90°C, then cooled to room temperature. A decant of 15000 gallons was taken to remove most of the remaining H₂SO₄. The remaining cesium alum plus spent ore was reslurried with

- 5 1400 gallons of water, heated to 90°C with agitation, and filtered through a filter press to remove the spent ore. A 300 gallon quantity of water at about 100°C was also sent through the filter press as a wash. The hot solution of cesium alum sulfate including water was evaporated to a volume of about 1300 gallons, and allowed to cool to room temperature. A decant of about 1000 gallons was taken. (first recrystallization
10 purification). The cesium alum was recrystallized a second time for further purification. The purified cesium alum was mixed and heated to between 80°C and 90°C with 1000 gallons water. A slurry of slaked lime comprising 264 pounds of calcium hydroxide in approximately 125 gallons of water was added to purified and heated cesium alum to raise the pH to greater than 9. Two liters of reagent H₂SO₄ was
15 added to adjust the pH to 8.5. The slurry was mixed approximately 1 hour at 80°C, cooled to about 60°C, and filtered. A second quantity of approximately 4 ponds of lime were added to obtain a pH >12. The Cs₂SO₄ liquor was evaporated to a approximately 300-400 gallons, and 15 pounds of Cs₂CO₃ was added to remove residual calcium as calcium carbonate. After the insoluble were filtered out the
20 Cs₂SO₄ solution was evaporated to a 50% solution. The overall yield was approximately 70%. The Cs₂SO₄ analyzed on a dry cesium sulfate basis contained:

	Rb	475 ppm
	K	38 ppm
	Na	165 ppm
25	Li	4 ppm
	Al	10 ppm
	Ca	7 ppm
	Cr	20 ppm
	Fe	5 ppm
30	Mg	<1 ppm
	Si	20 ppm

Example 6

This example illustrates the purification of cesium sulfate solution including

approximately 0.6 grams per liter calcium and approximately 0.1 grams per liter magnesium according to a process of the present invention. On a dry cesium sulfate basis, this represents approximately 7000 ppm calcium and approximately 1000 ppm magnesium.

- 5 Approximately 1600 gallons of dilute cesium sulfate solution (5-10% Cs_2SO_4) were mixed with 8 pounds of lime (slaked) to raise the pH from 7.4 to 12.8. The mixture was evaporated to a volume of 300-400 gallons, and the cesium sulfate liquor was decanted from settled precipitated solids. 18 pounds of cesium carbonate were added to precipitate residual calcium ions as calcium carbonate. The purified cesium
10 sulfate solution was filtered to remove residual $\text{Mg}(\text{OH})_2$ and CaCO_3 . The cesium sulfate was evaporated to a final volume of approximately 150 gallons. The final cesium sulfate liquor analyzed on a dry cesium sulfate basis had the following chemical make-up:

15	Ca	16ppm
	Mg	1ppm

Example 7

- 20 This example illustrates the purification of cesium formate solution including >5 grams per liter Sulfate, >1 grams per liter calcium, and approximately 0.05 grams per liter magnesium according to a process of the present invention. On a dry cesium formate basis, this represents >5% Sulfate, >1% Calcium, and approximately 600 ppm magnesium.
25 Approximately 1300 gallons of dilute cesium formate solution (5-10% CsCOOH) were mixed with 30 pounds of lime (slaked) to raise the pH from 7.1 to >12. The mixture was evaporated to a volume of approximately 500 gallons, and the cesium formate liquor was filtered to remove precipitated $\text{Mg}(\text{OH})_2$ and CaSO_4 . The cesium formate filtrate was heated to >60 °C and 110 pounds of $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ were
30 added. The precipitated BaSO_4 and $\text{Ca}(\text{OH})_2$ were removed by filtration. Residual soluble calcium ions were precipitated from the cesium formate filtrate as calcium carbonate by addition of 2 pounds potassium carbonate. The precipitated calcium carbonate was removed by filtration, and the cesium formate was evaporated to a specific gravity of approximately 2.3 g/ml (~82% cesium formate). A small amount of
35 90% formic acid was added to adjust the pH of the final cesium formate liquor to

between 8 and 9. The final cesium formate liquor analyzed on a dry cesium formate basis had the following chemical make-up:

Ca <10 ppm
Mg <1 ppm
5 SO₄ 200 ppm.

It should be clearly understood that the forms of the present invention herein described are illustrative only and are not intended to limit the scope of the invention.

WHAT IS CLAIMED IS:

- 1 1. A process for purifying a starting cesium compound which includes an ionic impurity comprising: calcium, sulfate, magnesium or mixtures thereof the process comprising: reacting impurities comprising calcium, sulfate, magnesium or mixtures thereof present in a solution including the solubilized starting cesium compound with suitable precipitating agents to form an insoluble precipitate including the impurity or impurities.
- 1 2. The process of claim 1 wherein the ionic impurities comprise sulfate and the precipitating agent comprises barium ion.
- 1 3. The process of claim 1 or 2 wherein the ionic impurities comprise magnesium and the precipitating agent comprises hydroxyl ion.
- 1 4. The process of claims 1-3 wherein the ionic impurities comprise calcium and the precipitating agent comprises hydroxyl ion.
- 1 5. The process of claims 1-4 wherein the ionic impurities comprise calcium and the precipitating agent comprises carbonate ion or carbon dioxide.
- 1 6. The process of claim 2-5 wherein the source of barium ion and hydroxyl ion comprises barium hydroxide.
- 1 7. The process of claim 2-6 wherein the source of carbonate ion comprises an alkali carbonate.
- 1 8. The process of claims 1-7 wherein the starting cesium compound comprises cesium formate, cesium nitrate, cesium chloride, cesium iodide, cesium bromide or cesium acetate.
- 1 9. The process of claims 1-8 wherein the starting cesium compound has been produced by a production process utilizing lime.

1 10. The process of claims 2-9 wherin the barium ions are added in an amount
2 approximately equal to the stoichiometric amount of sulfate ions in the solution
3 including the solubilized starting cesium compound.

1 11. The process of claims 3-10 wherein the hydroxyl ions are added in an
2 amount sufficient to raise the pH of the solution including the solubilized starting
3 cesium compound to 11.5 or above.

1 12. A process for purifying a starting cesium sulfate compound which
2 includes an ionic impurity comprising: calcium, magnesium or mixtures thereof the
3 process comprising: reacting impurities comprising calcium, magnesium or mixtures
4 thereof present in a solution including the solubilized starting cesium sulfate compound
5 with suitable precipitating agents to form an insoluble precipitate including the impurity
6 or impurities.

1 13. The process of claim 12 wherin the ionic impurity comprises magnesium
2 and the precipitating agent comprises hydroxyl ion.

1 14. The process of claims 12-13 wherin the ionic impurities comprise
2 calcium and the precipitating agent comprises hydroxyl ion.

1 15. The process of claims 12-14 wherin the ionic impurities comprise
2 calcium and the precipitating agent comprises carbonate ion or carbon dioxide.

1 16. The process of claim 13-15 wherin the source of hydroxyl ion comprises
2 an hydroxides of a metal selected from group 1A and 2A of the Periodic Table of the
3 Elements and mixtures thereof.

1 17. The process of claim 15-16 wherin the source of carbonate ions
2 comprises an alkali carbonate.

1 18. The process of claims 13-17 wherin hydroxyl ions are added in an
2 amount sufficient to raise the pH of the solution including the solubilized starting
3 cesium sulfate to 11.5 or above.

1 19. A cesium compound produced by the process of any of claims 1-11
2 comprising:
3 including less than 0.50% of a sulfate group, less than 0.3% of barium,
4 calcium, or magnesium including compounds, and less than 0.2% of other multivalent
5 cationic impurities.

1 20. A cesium compound produced by the process of any of claims 1-11
2 comprising:
3 less than 1000 ppm sulfate;
4 less than 1000 ppm calcium;
5 less than 1000 ppm barium; and
6 less than 1000 ppm magnesium.

1 21. A cesium sulfate compound produced by the process of any of claims 12-
2 18 comprising:
3 less than 0.3% of barium, calcium, or magnesium including compounds, and
4 less than 0.2% of other multivalent cationic impurities.

1 22. A cesium sulfate compound produced by the process of any of claims 12-
2 18 comprising:
3 less than 1000 ppm calcium;
4 less than 1000 ppm barium; and
5 less than 1000 ppm magnesium.

1 23. The process of claims 1-11 wherein the solution including the solubilized
2 starting cesium compound is produced by a process comprising:
3 treating a cesium-including material with a suitable reagent to dissolve
4 at least a portion of the cesium contained in the material and form a slurry comprising
5 cesium alum, cesium sulfate or cesium fluoride;
6 adding a base comprising slaked lime or calcium carbonate and an acid
7 including an anion of the desired starting cesium compound to the slurry comprising
8 dissolved cesium to form a solubilized cesium compound; and
9 separating the solubilized cesium compound solution in the presence of
10 the remainder of the starting cesium-including material.

1 24. The process of claims 12-18 wherein the solution including the solubilized
2 starting cesium sulfate is produced by a process comprising:
3 treating a cesium-including material with a suitable reagent to dissolve
4 at least a portion of the cesium contained in the material and form a slurry comprising
5 cesium alum;
6 adding a base comprising slaked lime or calcium carbonate to the slurry
7 comprising dissolved cesium to form a solubilized cesium sulfate compound; and
8 separating the solubilized cesium sulfate compound solution in the
9 presence of the remainder of the starting cesium-including material.

1 25. A fluid having a specific gravity of between about 1.2 g/cm³ and about
2 2.5 g/cm³ comprising: an aqueous mixture on a dry salt basis, comprising between
3 about 10 and 100% of a cesium formate including less than 0.50% of a chloride or
4 sulfate group, less than 0.3% of aluminum, barium, calcium, or magnesium including
5 compounds, and less than 0.2% of other multivalent cationic impurities.

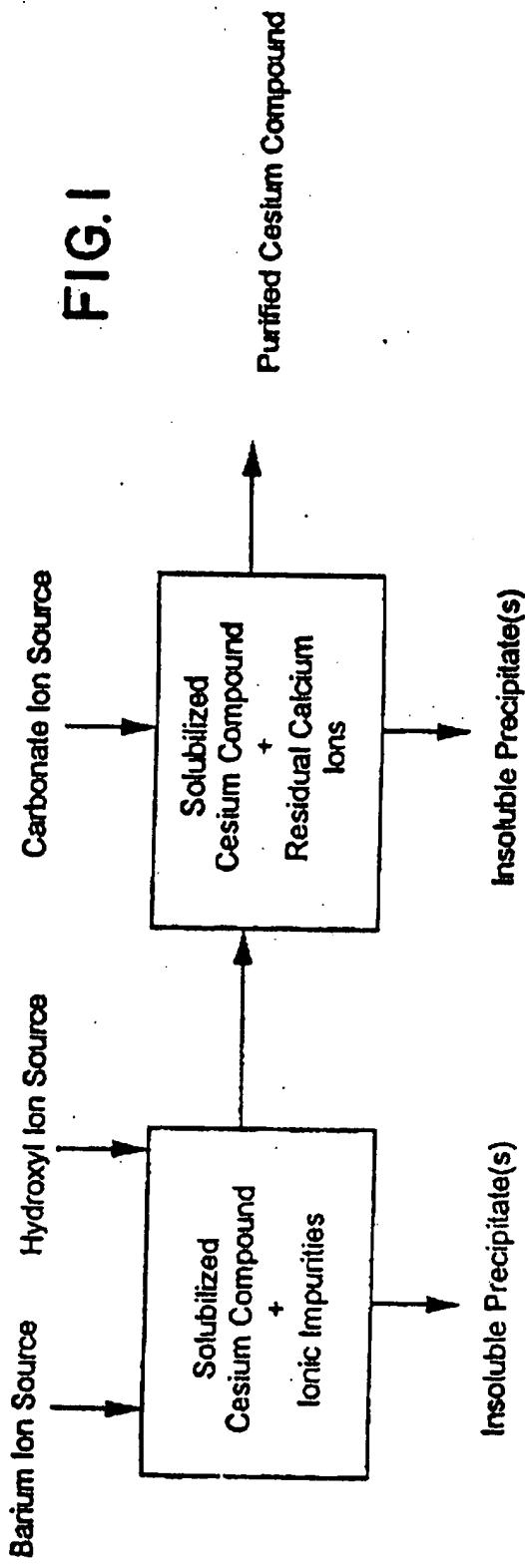
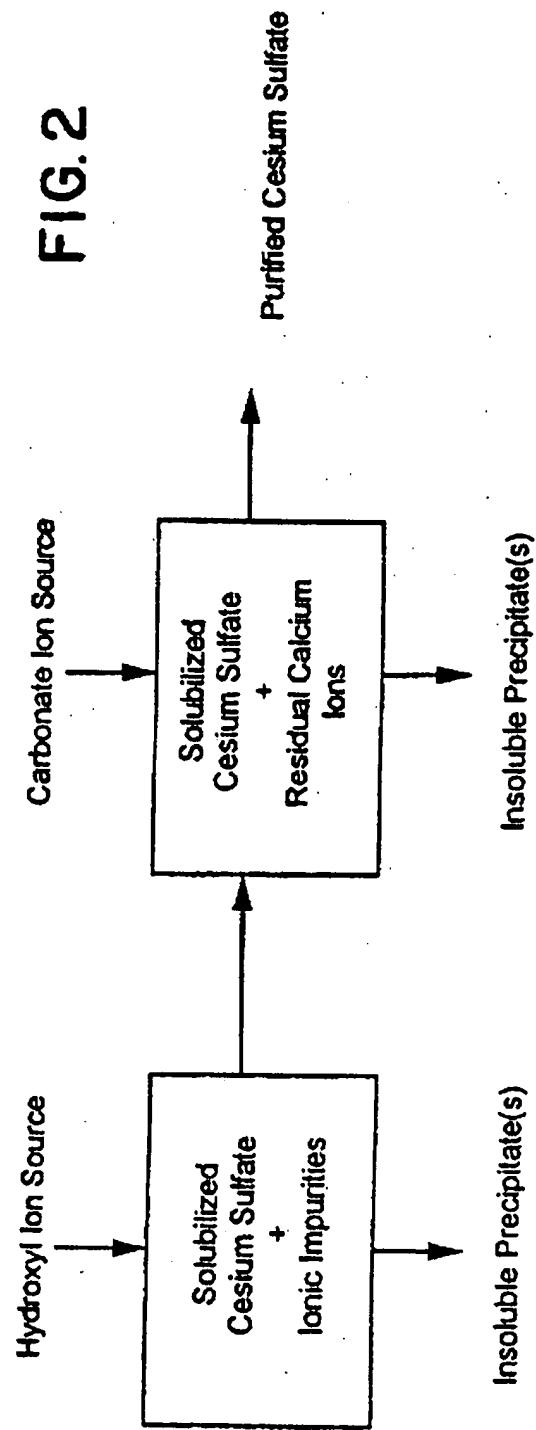
1 26. The fluid of claim 25 wherein the cesium formate comprises:
2 less than 1000 ppm sulfate;
3 less than 1000 ppm calcium;
4 less than 1000 ppm barium; and
5 less than 1000 ppm magnesium.

1 27. A drilling fluid in accordance with claim 25 wherein the cesium formate
2 and the fluid further comprises about 10 to 90% potassium formate and/or sodium
3 formate.

1 28. A drilling fluid in accordance with claim 27 wherein the formate
2 compounds are coformed.

1 29. A coformed mixture comprising a predetermined cesium compound
2 including less than 0.50% of a chloride or sulfate group, less than 0.3% of aluminum,
3 calcium, or magnesium compounds and less than 0.2% of other multivalent ion
4 impurities and a compound comprising a different metal and the anion of the
5 predetermined cesium compound.

- 1 30. In a process for producing a predetermined cesium compound wherein
- 2 a cesium-including material is treated with a suitable reagent to dissolve at least a
- 3 portion of the cesium contained in the material and form a slurry comprising cesium
- 4 alum, cesium sulfate or cesium fluoride, undissolved solids are separated from the
- 5 slurry and wherein a base comprising slaked lime or calcium carbonate and an acid
- 6 including an anion of the desired starting cesium compound are added to the filtrate
- 7 comprising dissolved cesium to form the predetermined cesium compound which
- 8 includes an ionic impurity comprising: calcium, sulfate, magnesium or mixtures
- 9 thereof, the improvement comprising:
- 10 purifying the cesium compound by reacting impurities comprising calcium,
- 11 sulfate, magnesium or mixtures thereof in a solution including the solubilized cesium
- 12 compound with suitable precipitating agents to form an insoluble precipitate including
- 13 the impurity or impurities.

FIG. 1**FIG. 2****SUBSTITUTE SHEET (RULE 26)**

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FIG. 3

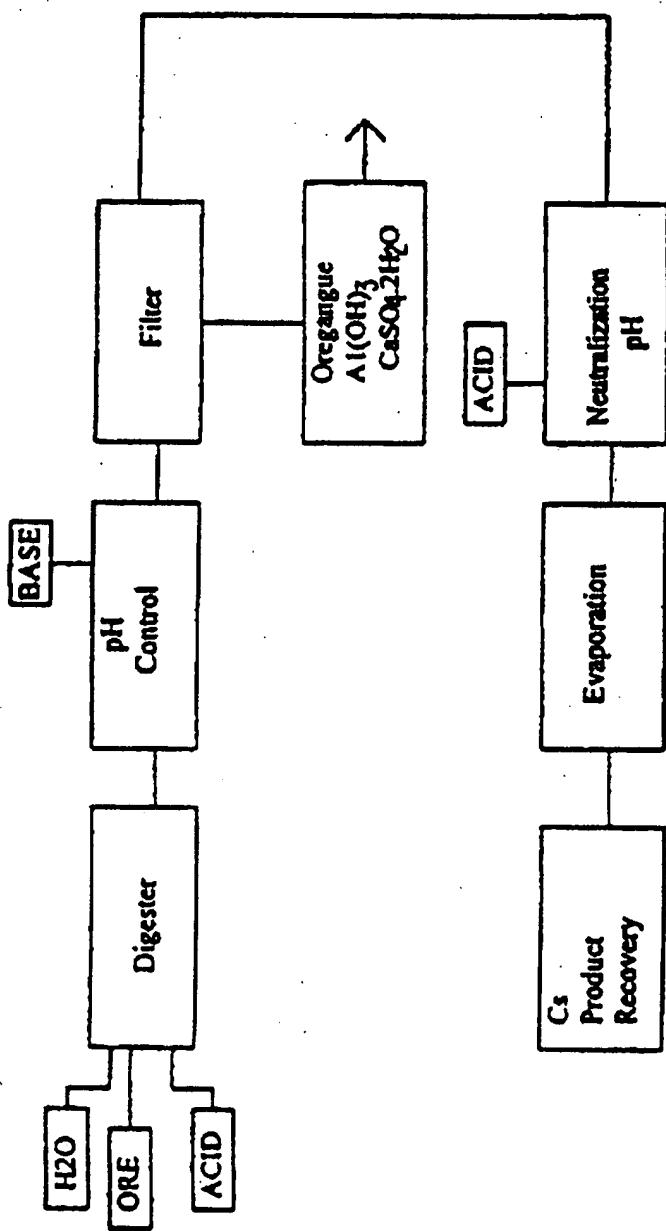
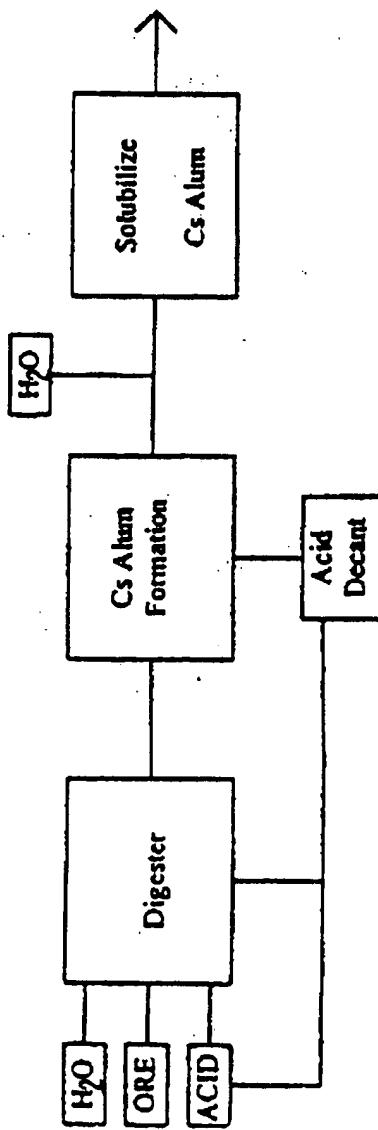


FIG. 4A



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FIG. 4B

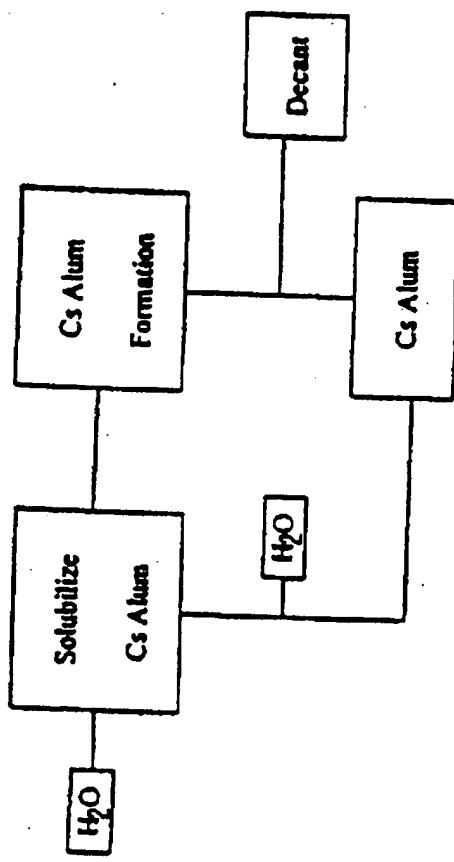
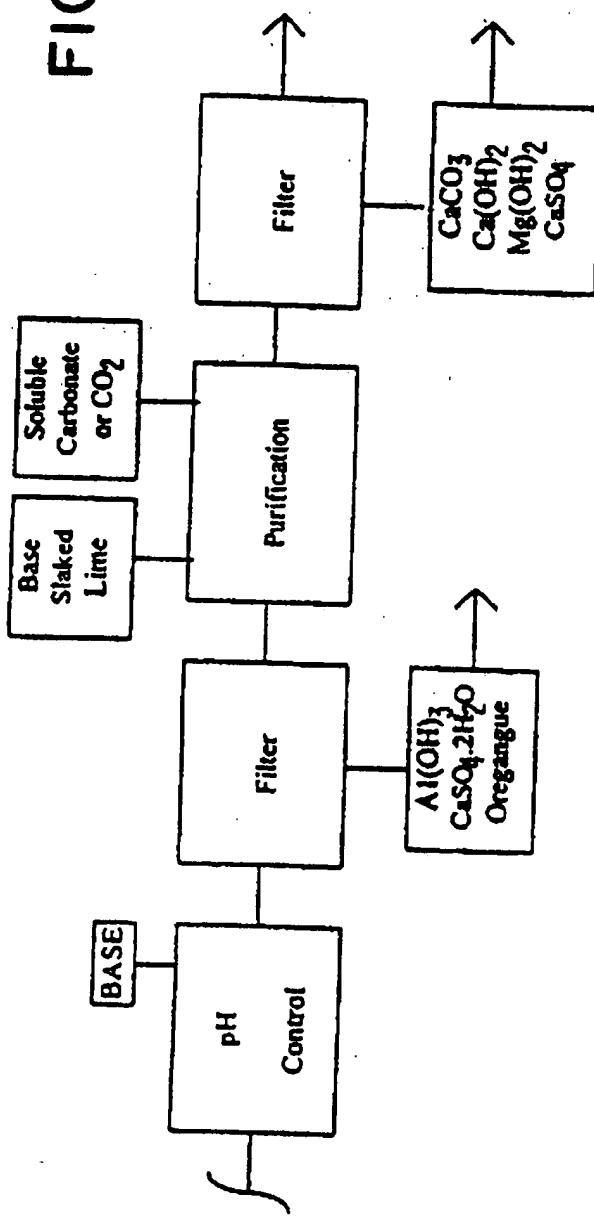


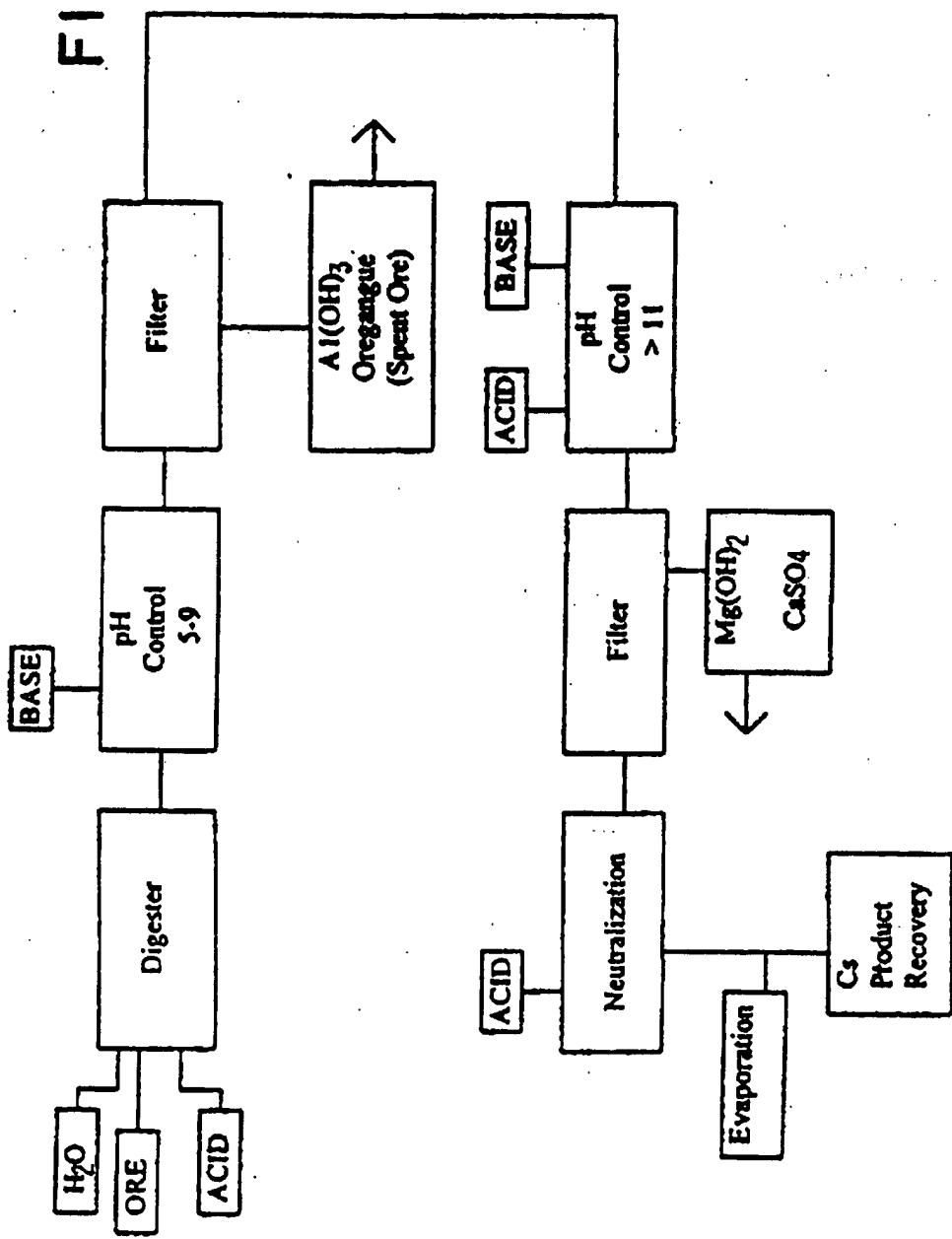
FIG. 4C



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FIG. 5



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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/04687

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01D17/00 C09K7/02 C07C51/41

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Character of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 207 571 (C.E.BERTHOLD) 21 September 1965 cited in the application see the whole document IDEM	1,2,6, 19-24,30
A		12
X	"Fluka 1995/96" , FLUKA XP002007924 see page 349 - page 352	19-22
X	EP,A,0 572 113 (BP CHEM INT LTD) 1 December 1993 cited in the application see the whole document	25-29

	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search 16 July 1996	Date of mailing of the international search report 19.08.96
Name and mailing address of the ISA European Patent Office, P.O. 5818 Patentdienst 3 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax (+31-70) 340-2016	Authorized officer Van der Poel, W

INTERNATIONAL SEARCH REPORT

Int'l. Appl. No.
PCT/US 96/04687

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 489 509 (JOHNSON IRWIN E) 13 January 1970 see the whole document ----	1-3,5,8, 9,19-24, 30
A	DE,C,43 13 480 (METALLGESELLSCHAFT AG) 14 April 1994 cited in the application see the whole document -----	1,9,23, 30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/04687

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-3207571	21-09-65	NONE		
EP-A-0572113	01-12-93	DE-D-	69300541	02-11-95
		DE-T-	69300541	21-03-96
		NO-A-	931495	30-11-93
US-A-3489509	13-01-70	NONE		
DE-C-4313480	14-04-94	AU-B-	6679294	21-11-94
		BR-A-	9406214	09-01-96
		CA-A-	2161245	10-11-94
		WO-A-	9425422	10-11-94
		EP-A-	0695286	07-02-96
		FI-A-	955049	23-10-95
		HU-A-	72014	28-03-96
		NO-A-	954134	17-10-95
		PL-A-	311231	05-02-96
		ZA-A-	9402813	23-10-95
		ZW-A-	4994	23-11-94